

UGK-101 #131

MLM-2563

EGSP
OPEN FILE

**Geochemical Evaluation of the
Eastern Gas Shales - Part 1**

Richard D. McIver and Ronald E. Zielinski

September 29, 1978



Monsanto

FOUNDER

MONSANTO RESEARCH CORPORATION

U.S. DEPARTMENT OF ENERGY

This report was prepared as an account of work sponsored by the United States Government. Within the United States, for the United States Department of Commerce, neither the United States nor the United States Department of Commerce, nor any of their employees, nor any of their contractors, subcontractors, or agents, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy or completeness of any information, advice, or other instructions disclosed herein, or for the results of any use of the information contained herein.

PRINTED IN THE UNITED STATES OF AMERICA

Available from:
National Technical Information Service
U.S. Department of Commerce
5200 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$4.50; Microfilm \$3.00

Geochemical Evaluation of the Eastern Gas Shales - Part 1

Richard D. McIver and Ronald E. Zielinski

Issued: September 29, 1978

MOUND FACILITY

Miamisburg, Ohio 45342

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

Contents

	<u>Page</u>
SUMMARY	3
INTRODUCTION.	5
GEOGRAPHIC AND GEOLOGIC SETTING	6
GEOCHEMICAL DATA.	11
STRATIGRAPHY AND BIOFACIES.	11
ORGANIC CARBON.	16
KEROGEN DESCRIPTIONS.	16
KEROGEN ALTERATION INDICES AND VITRINITE REFLECTANCE.	22
CORE GAS ANALYSIS	23
C ₁₅ + HYDROCARBON CONTENTS	26
CARBON ISOTOPE RATIOS	30
FUTURE WORK	31
REFERENCES.	31
DISTRIBUTION.	33

Summary

Although the Late Devonian-age dark shales of the Eastern Interior Basins are thought to be uniformly gassy, organic geochemical studies in the Appalachian and Illinois Basins show that the gas is not uniformly distributed and that most of the gas is probably sourced and largely retained in thin, organic-rich zones that were deposited in restricted marine environments. These restricted conditions occurred intermittently as the basins subsided and the structural highs were periodically uplifted and shed their sediments and detrital organic matter. As the Devonian-age basins filled, the environments of deposition of the Appalachian Basin and Illinois Basin became non-marine more and more northerly and northwestwardly, respectively.

Heavy hydrocarbon-to-organic carbon ratios show that the organic matter associated with the restricted marine environments is different in the two basins, perhaps because of their relative positions with respect to their connections to the open oceans. During virtually the entire period in question, the Appalachian Basin had a direct connection; the Illinois Basin was somewhat isolated by the already developing Cincinnati Arch on the east and the Kankakee or Wabash Arch on the north. However, the differences in organic matter noted in this study suggest a northwest connection of the Illinois Basin to a different ocean mass than that which supplied marine waters to the Appalachian Basin.

In addition to two chemically distinct rich-organic facies associated with the restricted marine environments in the two basins, there is still another rich facies associated with the nonmarine sediments filling the Appalachian geosyncline from the growing mountains on the east. This organic facies is very gassy also, but the gas contains less of the higher homologs of methane. In contrast, the gases generated by the two other organic facies are rich in heavier hydrocarbon gases and therefore are higher B.T.U. gases.

As a fossil fuel resource, certain facies within the dark Devonian-age shale are much richer gas sources than others. To optimize the development of this resource, results of this organic geochemical study suggest that the most prolific potential reservoirs (naturally occurring or induced) should be sought or located in the geologic section containing or contiguous to the richest organic source intervals; i.e., rocks deposited in restricted

marine environments. This should be stressed, because the section is not uniformly gassy. The amount of gas in rocks of each interval depends directly on the amount of detrital organic matter, which is quite variable. Moreover, it appears that virtually all the gas as well as virtually all the liquid hydrocarbons are retained in the rock where they were generated.

Introduction

The Late Devonian-age dark shales of the Eastern Interior Basins contain a prodigious amount of natural gas underlying thousands of square miles of the United States. This potential gas source is of great economic interest because of its proximity to major concentrations of energy-consuming industrial and population centers. However, the gas is so tightly held in the shale's low-permeability, low-porosity pore network that it does not currently constitute an economically attractive drilling target for gas explorationists or producers. The United States Department of Energy, Morgantown Energy Technology Center, through its Eastern Gas Shale Project is stimulating the search for viable methods to utilize this valuable natural resource and help alleviate a growing shortage of domestic natural gas. An important part of the comprehensive program is Mound Facility's research into the characterization and distribution of the gas and its source, or sources. A detailed chemical measurement and characterization of the organic matter in the dark shale unit, along with many of the important ancillary geological measurements necessary for a complete resource assessment, are currently in progress. On selected samples the following determinations are made:

C₁ through C₇ hydrocarbon gases contained in cores canned shortly after retrieval at the well site;

Lithological descriptions of the rock material;

Clay mineral content;

Rock age and geological setting (environment) at time of deposition by study of small fossils (palynology);

Organic carbon content;

Individual C₄ - C₇ hydrocarbons;

Solvent-soluble bitumen - with separation into important component fractions by column chromatography;

C₁₅ + paraffin - naphthene hydrocarbon distributions by gas chromatography;

Characterization of solvent-insoluble organic matter (kerogen) - visual description, elemental composition, and carbon-isotope composition;

Vitrinite reflectance for an estimate of thermal history of the rock;

Oil and other volatiles generated by heating (material balance assay and thermal extraction analysis) and characterization of gaseous and light liquid hydrocarbon products; and

Organic carbon fraction involved in oil and gas generation (material balance assay and C-H-N analyses).

These parameters give a number of independent and dependent variables from which the geologic and chemical conditions at the time of deposition of the rocks can be elucidated. Moreover, they provide a comprehensive inventory of the

organic matter remaining in the rocks. Some of these parameters are important in outlining the role of the rocks in sourcing the gas that is now being sought; some will undoubtedly be important in future exploitation schemes in which more than combustible gas is being sought (e.g., chemical feedstocks).

This publication is a status report on some interesting findings to date and their potentially important implications. The interpretation is preliminary because it is based on results from some of the analyses of samples that cover but a small fraction of the study area. However, it appears to be firm enough to provide an integrated geological and geochemical model that can be expanded, tested, and modified as more data become available.

Geographic and geologic setting

The overall study area, in which the Late Devonian-age dark shales exist and have potential as a source of natural gas, is shown on the map in Figure 1. The basins are located by dashed outlines. However, it should be noted that the arbitrarily chosen boundaries correspond to the outermost occurrences of Silurian-age sediments for the Appalachian and Michigan Basins. For the Illinois basin, the outline corresponds roughly with the outermost occurrence of Pennsylvanian-age rocks. If older rocks were chosen in any of the basins, the outlines would be larger, and the positive structural features between them thinner. Other structural features are also shown on the map, as is the general location of the axis (deepest part) for the Appalachian Basin during Late Devonian time.

The wells from which samples were obtained and studied are also located on the map, and more information on their locations is given in the map key (Table 1). The two lines of section shown later in the report are also indicated. Note that the line of section for the Illinois Basin, section A - A', zig-zags sharply at Wells P-1 and I-1; this was done so that the wells appear on the section in the order of their location with respect to basin position. The deepest part of this basin at the time of deposition of the dark shale was between Wells I-1 and O-1. As the map indicates, the deepest part of the Appalachian Basin in Late Devonian time, along the section B - B', occurs between Wells KY-2 and VA-1. Because Wells CW-A and CW-B are so close geographically and in similar geologic settings, they are presented on the cross-section as but one well.

The general basin configuration during late Devonian time is shown diagrammatically in Figure 2. This represents one of the later episodes in a 250-million year history of deposition in the Eastern United States as the Appalachian mountains were repeatedly uplifted and as they exposed increasingly younger rocks once deposited in the persistent geosyncline. There was an inexorable westward progression of the mountain axis and the center of deposition of the basin. The thickness and volume of sediment also decreased with each succeeding geologic age, from as much as 20,000 ft of pre-Devonian rocks to less than a third of that thickness in the Devonian period.

From their axes of deposition, the Paleozoic sediments thin westward. Perhaps as

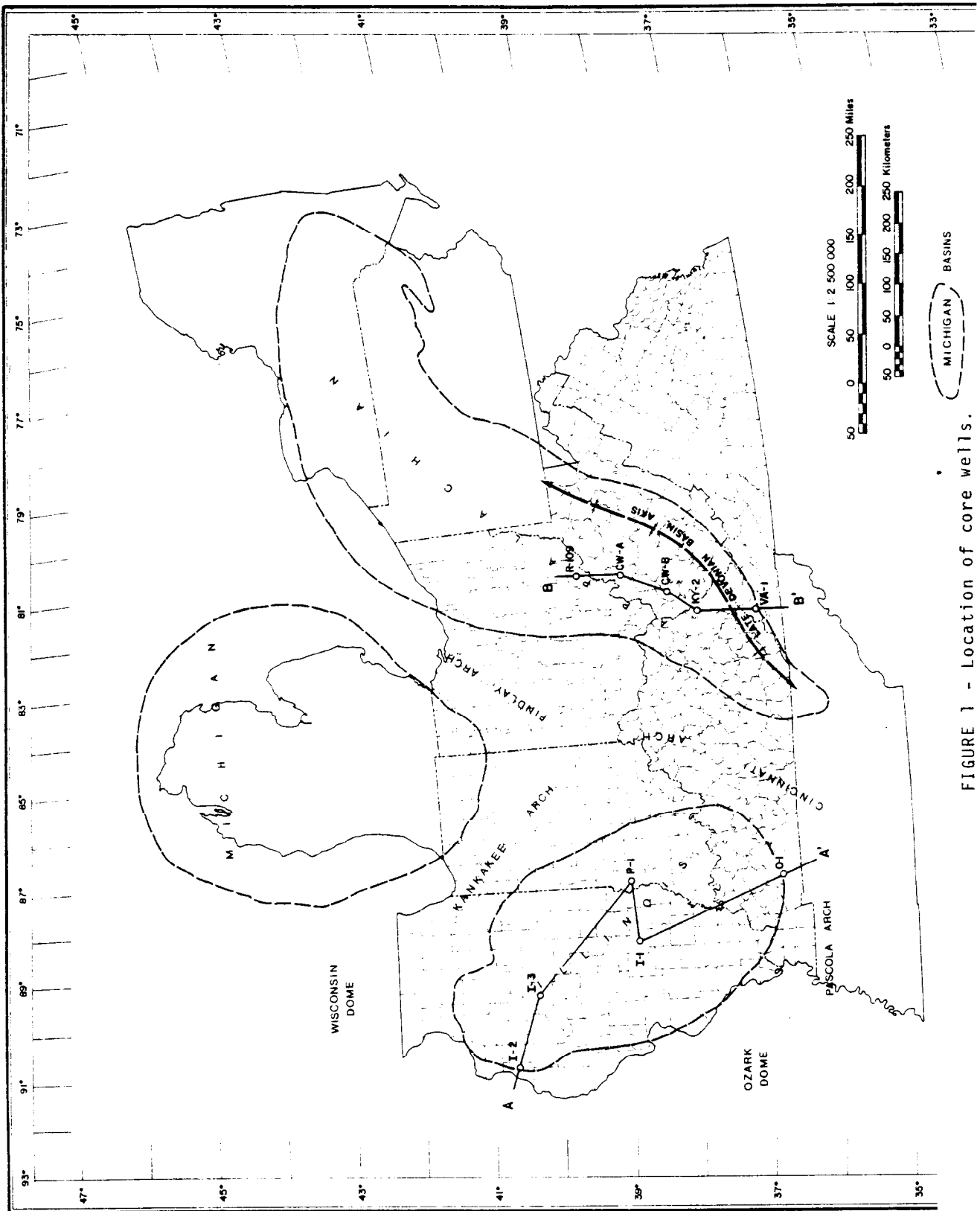


FIGURE 1 - Location of core wells.

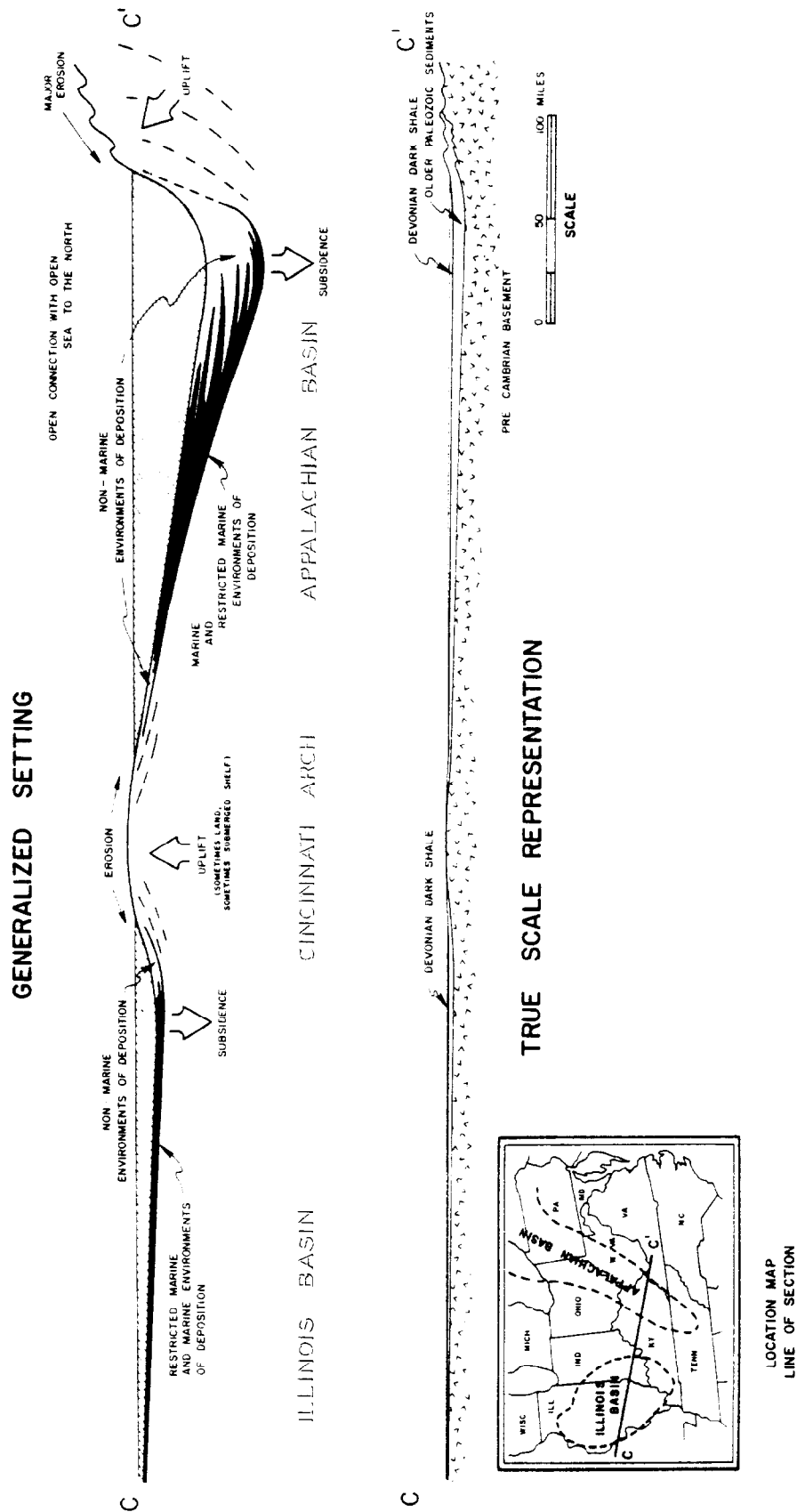


FIGURE 2 - Diagrammatic geological setting Appalachian and Illinois basins.

Table 1

WELLS INCLUDED IN THIS STUDY

Illinois Basin

- I-2 Henderson County, Illinois
Northern Illinois Gas No. 1 RAR 32-8N-4W
- I-3 Tazewell County, Illinois
Northern Illinois Gas No. 1 MAK 8-23N-2W
- P-1 Sullivan County, Indiana
Energy Resources of Indiana No. 1 Phegley Farms
14-6N-10W
- I-1 Effingham County, Illinois
Tri-Star Producing No. 1-D Lancaster 31-9N-4E
- O-1 Christian County, Kentucky
Orbit Gas No. 1 Ray Clark 12-G-25

Appalachian Basin

- R-109 Washington County, Ohio; Warren Township Sec 27
River Gas No. R-109 F. L. House
- CW-A "Cottageville Wells" Jackson County, West Virginia
Consolidated Gas Supply No. 11940 L. A. Baler
and No. 12401 W. L. Pinnell
- CW-B "Cottageville Wells" Lincoln County, West Virginia
Columbia Gas Transmission No. 20402 and No. 20403
- KY-2 Martin County, Kentucky
Columbia Gas Transmission No. 20336
- VA-1 Wise County, Virginia
Columbia Gas Transmission No. 20338

early as late Cambrian, and certainly by Ordovician time, the thenceforth persistent Cincinnati Geanticline (Arch) appeared and the Illinois Basin, as such, took shape. This basin is a gently down-warped, shallow depression bounded by broad, low-relief domes and arches, most of which were positive features by late Ordovician time and were intermittently slightly emergent or slightly awash from then on through the remainder of the Paleozoic Era. Although the diagram serves to illustrate the basin geometry, it is highly exaggerated, as are the sections on which the geochemical data are presented. For a clearer visualization of the true basin geometry, at the

bottom of Figure 2 there is a cross-section showing the relative thickness of the sedimentary section with respect to basin width. The approximate position of the dark shales is also shown, but the thickness of the line representing them is in actuality too thick. Therefore, this figure clearly shows that, on a broad regional basis, the basins are not deep depressions at all, and the dark shales are relatively shallow and very thin.

A generalized stratigraphic section is also included, on Figure 3, in order to show the relative geological position of the dark shale section and some of the terminology (e.g., Famennian and

GENERAL CLASSIFICATION							NORTH AMERICAN CLASSIFICATION			
Approx time (10 ⁶ yrs)	Erathem Era	System Period	Series Epoch	Stage / Age						
270	P	Permian	Upper	Tartarian	(Djulfian)			Ochoan		
			Late	Kazanian	(Penjabian)					
			Middle	Kungurian						
			Lower	Artinskian						
		Carboniferous	Early	Sakmarian					Leonardian	
				Stephanian (Uralian)				Virgilian		
			Silesian	Westphalian (Moscovian)	D		Pennsylvanian	Missourian		
					C			Desmoinesian		
					B					
					A			Atokan		
Late	Namurian				Morrowan					
	Lower		Dinantian	Viséan		Mississippian	Chesterian			
Tournaisian							Meramecian			
350	a		Early						Osagean	
		Upper	Famennian	Strunian	Etreungtian		Kinderhookian			
				Late	Frasnian				Bradfordian	
		Middle	Givetian				Chautauquan			
							Couvinian		Senecan	
		Lower	Early	Emsian			Erian			
				Sieganian						
		400	z	Devonian	Early	Gedinnian			Ulsterian	
						Downtonian				
Salopian	Ludlovian						Cayugan			
	Wenlockian						Niagaran			
Silurian (Gothlandian)				Llandoveryan			Albion			
				Ordovician	Upper	Ashgillian			Gamachian	
Caradocian							Richmondian			
Lower	Llandellian						Maysvillian			
	Llanvirnian						Edenian			
450	c			Ordovician	Early	Arenigian (Skiddavian)			Champlainian	Trentonian
		Tremadocian					Blackriverian			
								Chazyan		
		Upper	Potsdamian				Croixian	Trempealeauian		
								Late	Acadian	
								Dresbachian		
								Middle		Albertan
		600	Precambrian	Cambrian	Lower	Georgian				Waucoban

FIGURE 3 - Stratigraphic section showing rock series studied.

Frasnian) used in the area and in this report. For the sake of uniformity in this presentation, the dark shales will be called just that, without the use of names that vary from locality to locality.

Geochemical data

This report is a synthesis of some of the data that have been reported in earlier reports [1-4] and presentations [5-8]. Tabulations of their large data sets will not be duplicated here because they are available in the original documents. In preparation for this report, much of those data were correlated graphically, one variable against another; important ones were plotted individually and as ratios on maps and cross-sections. After these exercises, certain parameters emerged as important in delineating distinctly different organic matter types, herein called organic facies, and some revealed somewhat interesting, unexpected geochemical relationships. Further study of additional samples, particularly more closely spaced samples within the wells studied, will undoubtedly reveal more chemical parameters important not only in the recognition of the resource quality and quantity but also in optimizing locations and procedures for exploitation.

The analytical procedures, too, were described in detail in the earlier reports and will not be discussed again herein, save for a few general descriptions, some of which were already presented in the Introduction.

Stratigraphy and biofacies

With the usual heterogeneity of rocks, and possible recurrence of similar geological and geochemical conditions in a

depositional basin, it is important in a study such as this to ascertain whether the analyses are being made on correlative rocks; i.e., were the sediments deposited at the same time, and/or in identical depositional environments. This can help ensure that the target interval was not missed and that complete coverage was obtained. Usually, the best correlations are accomplished with a suite of down-hole probes from which are derived logs (well logs) on which the responses of the rocks; i.e., electrical, sonic, physical, etc., provide characteristic patterns that can be recognized, compared, and correlated from well to well. Similarly, the characteristics (i.e., rock type, grain size distribution, clay mineral content, fossil contents, etc.) of the rock (cores or cuttings) collected as the well proceeds will generally give excellent correlations. In this study, the correlations were all based on biofacies and chemical similarities.

Some of the rock samples from some of the wells were treated with mineral acids to remove much of the silicate and carbonate matrices, and their organic remains were studied under the microscope by a palynologist, experienced in looking at rocks from this area, to determine the age of the rocks and the environmental conditions under which the rocks were deposited.

The determination of the age of the rocks, Late Devonian, and the subdivision into its Famennian and Frasnian stages, were possible because of the distinctive morphology of spores and acritarchs preserved in the rocks. The environment of deposition was determined by the relative proportion of polymorphs known to be common in nonmarine, restricted marine,

and marine environments. In most samples, representatives of all three types were present, so the interpretation was based on the most abundant forms after a large number, usually 200 to 300, were counted on a slide. Also, there frequently was an abundance, even a predominance, of older, apparently more thermally altered, material. Obviously, this was organic matter laid down in older Paleozoic (including earlier Devonian) rocks that had subsequently been buried, uplifted, and eroded - with their products filling the active basin (see Figure 2).

The general depositional relationships from these studies are presented in Figures 4 and 5. Insofar as possible, these cross sections are hung on the Frasnian-Famennian time boundary (see Figure 2), and the results of the palynological study on four wells are represented diagrammatically. Palynological results were not available on Well I-1, but it has been tentatively placed in its relative position based on interpretation of the chemical information to be discussed later. Samples from Wells I-2 and I-3 from the shelf margin on the northwest edge of the basin were all of Famennian age, but how far above the Famennian-Frasnian boundary cannot be determined from the data.

The lowermost samples of both these wells were deposited in a marine environment which indicates the existence of a shallow sea in this area receiving only fine-grained inorganic material from a sediment-source area a great distance away. There was apparently free connection and circulation of waters to and from the deeper open sea, also quite far away, probably to the northwest and perhaps to the northeast. For a time, the free

connection to the open sea was gradually restricted, perhaps by local bottom topography, and then was restored. (While these episodes have been correlated in these two wells, they may actually be similar but different cycles in a repeated series of cycles that often occur in a basin's history.)

While the restored open marine conditions and circulation prevailed, nearly a hundred feet of marine sediment was deposited. No more of the record is available at the I-3 well, but at I-2, there was subsequently a relatively abrupt change from marine to nonmarine conditions as the basin filled and connection with the open sea was disrupted, and/or as streams of the boundary land masses carried increasing amounts of nonmarine clastic sediments into the basin.

At the basin position of Well P-1, the environment was restricted marine at the Famennian-Frasnian boundary and became nonmarine in the uppermost sample. This change from restricted marine to nonmarine probably occurred earlier at this basin position because of the presence of the Cincinnati Arch that was intermittently being uplifted and was shedding nonmarine clastics into the Devonian basin. In this basin position, closest to the Arch, nonmarine conditions probably persisted for most, if not all, of the remainder of the Late Devonian Period as regression of the seas to the northwest continued.

The Devonian rocks in Well I-1 were deposited in the deepest part of the Illinois Basin represented in our study. The five samples cover a stratigraphic interval of only 76 ft but, because of their very high organic carbon contents (to be discussed later), they were assumed to be deposited in a restricted marine

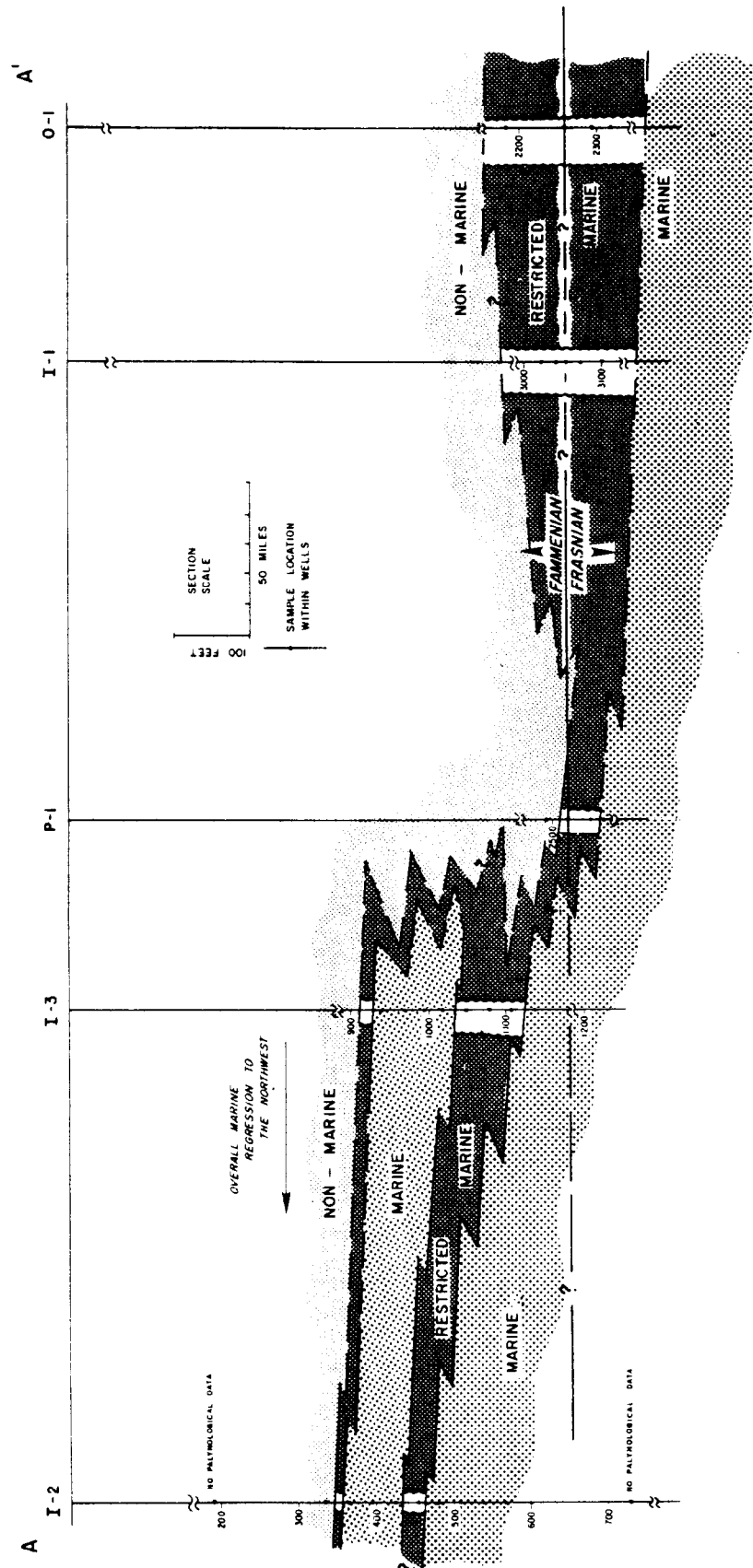


FIGURE 4 - Environmental interpretation - Illinois Basin based on biostratigraphic in Wells I-2, I-3, and P-1 and organic geochemistry in Wells I-1 and 0-1.

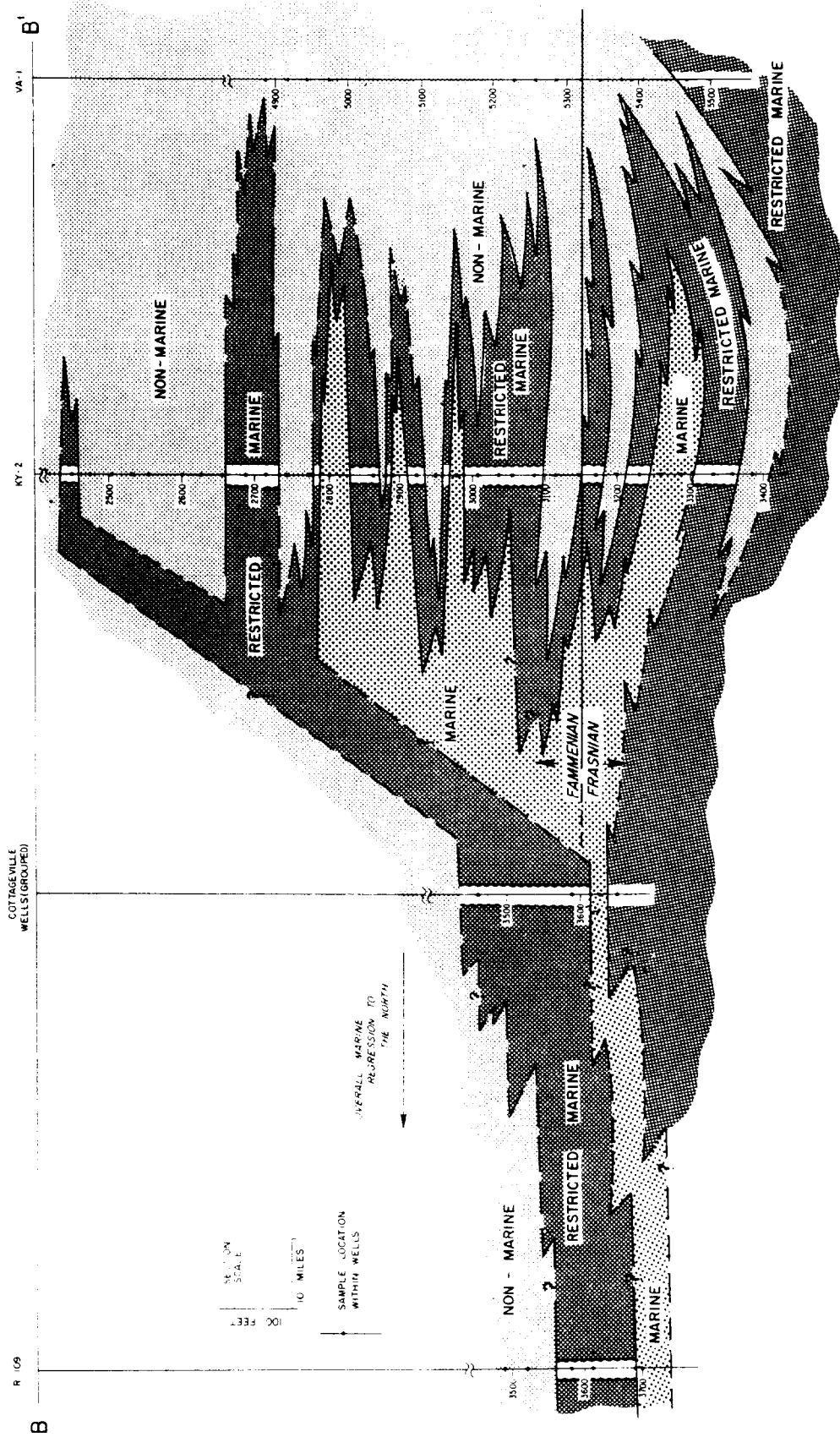


FIGURE 5 - Environmental interpretation - Appalachian Basin based on biostratigraphy in Wells KY-2 and VA-1 and organic carbon contents in R-109 and Cottageville wells.

environment and probably just about at the Frasnian-Famennian boundary, as indicated in the interpretive cross section.

Well O-1 is on the southern shelf of the basin in sediments that thinned gradually to the south. The Frasnian-Famennian boundary was bracketed by the samples and all were deposited in restricted marine conditions, although scanty details from the palynology indicate that the oldest sample, while restricted marine, is more marine than the other, younger ones. This is in agreement with the overall picture of a marine regression to the northwest in this basin.

The data on samples from wells in the Appalachian Basin (Figure 5) also are consistent with a marine regression to the north; in this case, apparently as the long narrow marine waterway to the open oceans to the north was slowly filled and/or uplifted. Samples from the southernmost well in this basin were all deposited in a nonmarine environment, with the exception of the oldest one. Thus, the influence of the growing Appalachian mountains completely dominates the sedimentation in this basin area, from 150 ft below the Frasnian-Famennian boundary to 400 ft above it.

From Well VA-1, the line of the cross section crosses the basin axis (deepest part) which has not yet been sampled. The setting of Well KY-2 on the other (western) shelf is a classic example of conditions at a basin hinge-line: sometimes the marine influence from the north dominates; sometimes the circulation, and hence the environment, is restricted; and sometimes, with uplift of high-relief Appalachian mountains proceeding relatively more rapidly than corresponding

subsidence of the geosyncline, the non-marine clastics pour from the mountains, cross the depocenter, and are carried long distances northwestward, at times even across much of the shelf.

At the position of the Cottageville wells, the environments were not determined palynologically, but they also probably varied from marine to nonmarine and were apparently persistent over longer time periods than at KY-2. The organic geochemistry suggests at least two cycles of restricted-marine depositional environments, with at least one short marine cycle (represented by but one sample, at 3625', in one well.) The age of the sediments is undetermined but could be placed either above or below the Frasnian-Famennian contact.

At the position of the northernmost well analyzed to date, R-109, the palynology was not done, but from the geochemistry, it appears that there is one restricted marine cycle with marine deposition above and below. This interpretation agrees with the regional geology that indicates an open connection to the sea to the northeast throughout the late Devonian.

Thus, the palynology, supplemented by the organic geochemistry, gives a geologically reasonable interpretation; i.e., of a marine environment slowly and reluctantly regressing northward as non-marine sediments were shed from highlands and filled the basins more rapidly than they subsided. The influence of the connection to the open oceans to the north was snuffed out only slowly; and as mountain growth occasionally slowed or basin subsidence accelerated slightly, the marine waters swept southward again only to have the dominant influence of

the highlands restored. First restricted marine, and then nonmarine, environments of deposition were re-established and persisted for longer and longer periods as the Devonian system came to a close.

Organic carbon

In geochemical studies, organic carbon content is the single most useful parameter in revealing overall hydrocarbon source potential although alone it reveals nothing about the relative potential for oil versus gas. On Figures 6 and 7, which are cross sections on the same scale as Figures 4 and 5, organic carbon contents are plotted at the appropriate positions down the wells. When the two sets of data are superimposed, in wells in which both biostratigraphy and organic carbon contents are available, particularly at Well KY-2, the Cottageville Wells, Well R-109, Well I-3, and Well P-1, there is a remarkable close association of high organic carbon contents with restricted marine environments of deposition, and low organic carbon contents with both marine and nonmarine environments. Therefore, the biostratigraphic reconstruction can be done with both sets of data; in wells in which only organic carbon data are available, the environment can be inferred.

One apparent exception is at Well VA-1, in which three cycles of high organic carbon are associated with nonmarine deposition. However, these highs provide the key to the interpreted proximity of restricted-marine sedimentary wedges (Figure 2). In Wells I-2, I-3, and KY-2, organic carbon contents reach maxima in the restricted environment but increase both before and after restricted

conditions become dominant, i.e., in some of the marine and some of the nonmarine facies contiguous to the restricted marine facies. Therefore, the three cycles of organic carbon enrichment in Well VA-1 strongly suggest that the nonmarine setting was at least being influenced by restricted marine conditions relatively close by, although not strongly enough transgressive to dominate the sediments - at least not in the intervals sampled - but perhaps in intervening ones.

Together, the biostratigraphy and organic carbon data present a very consistent pattern, shown diagrammatically in Figure 2: the emerging Appalachians were a continuous prolific sediment source, and the intermittently positive Cincinnati Arch was an occasional one, as both basins filled in Late Devonian time and as the once-free marine circulation from the north-northeast in the Appalachian Basin and the north-northwest in the Illinois Basin gradually disappeared, and non-marine conditions covered most, if not all, the basin for a time at the close of the Devonian Period.

Kerogen descriptions

Along with the distribution of organic carbon in a section or a basin, another basic parameter is the nature of the detrital organic matter. One approach in studying this parameter is purely descriptive; i.e., a visual description of the acid and solvent insoluble organic matter under the binocular microscope. Sedimentary kerogen is primarily composed of remnants of algal, amorphous (sapropel), herbaceous (spores, pollen, cuticles, and membrane debris) material; structured material (called "woody"); and



FIGURE 6 - Organic carbon contents - Illinois Basin Kerogen Facies (see Figure 8), HC/OC Facies (see Figure 11).

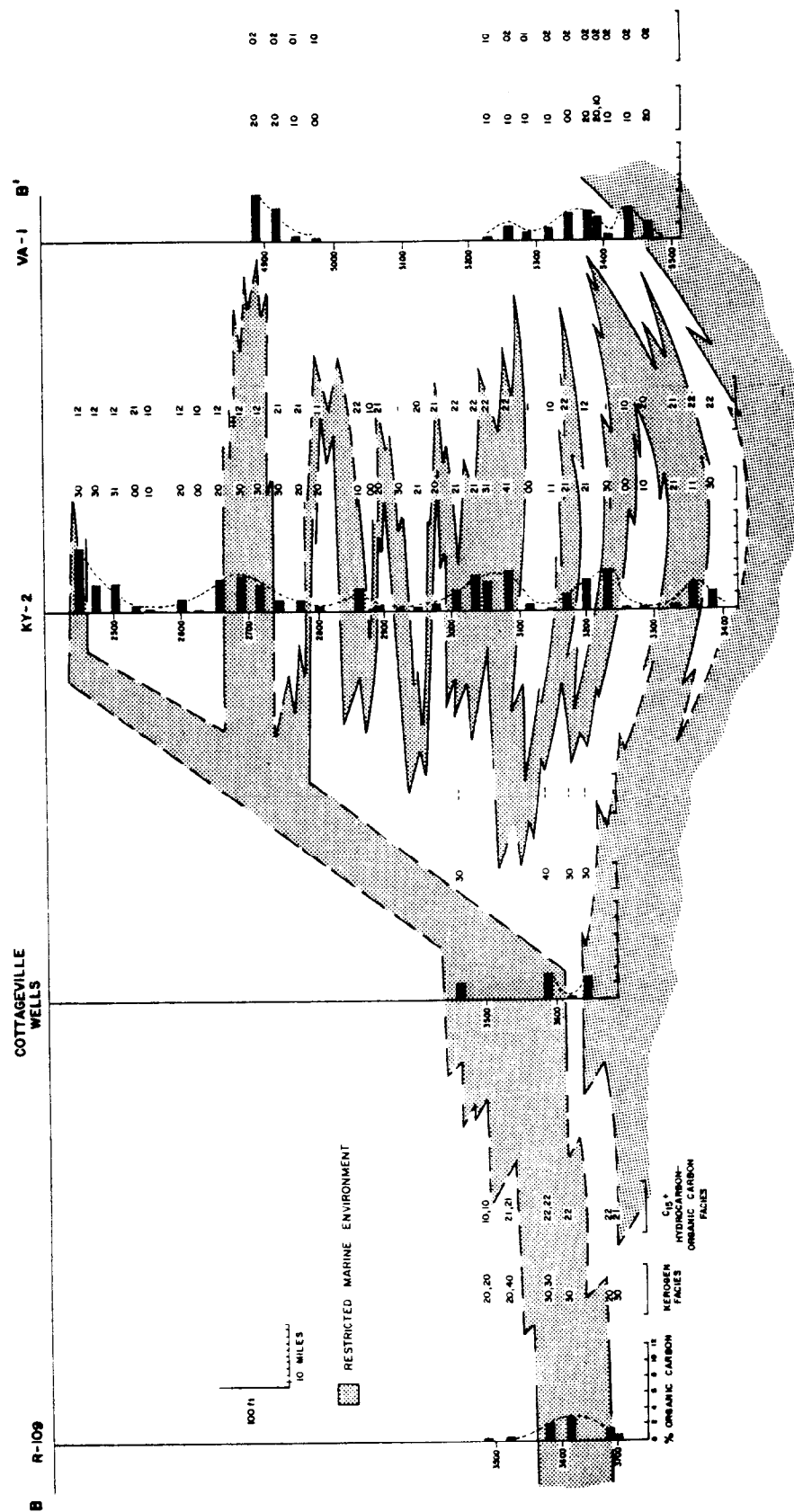


FIGURE 7 - Organic carbon contents - Appalachian Basin Kerogen Facies (see Figure 9), HC/OC Facies (see Figure 12).

finely divided coaly (inertinite) material. A great volume of literature to date agrees that, on a unit-volume basis, the algal and amorphous material is far-and-away the most prolific oil-producer; the herbaceous is intermediate; and the woody and coaly types are mostly gas-generating, as the kerogens are subjected to temperatures that increase with depth of burial and over the long time periods associated with the rocks' history.

In order to help visualize the distribution of organic facies in the study area, the kerogen description data were plotted on triangular diagrams - 100% algal and amorphous at one apex, 100% herbaceous at another, and 100% woody and coaly at the third. Figures 8 and 9 show the results of these plots for the Illinois and Appalachian Basins, respectively. The envelopes that include all the data are drawn for each well to show the trends - the individual data points have been deleted to simplify the drawings for this interpretive report. The facies are divided into nine arbitrary types with numerical designations ranging from 00 through 40 and 11 through 41; the larger the first numeral the more oily the organic matter. The appearance of the numeral "1" in the second position indicates greater than 50% herbaceous kerogen. The arbitrary facies designations are plotted in their appropriate positions in the cross sections (Figures 6 and 7) to show the stratigraphic and regional trends.

These plots further strengthen the interpretation that there were several distinct organic facies existing at different times in different parts of the basin. In the Illinois Basin, the kerogen facies

(Figure 8) fit the biostratigraphy and organic stratigraphy, Figure 2. Samples from areas of Wells O-1, I-1, and part of those from P-1 and I-2 contain a paucity of woody-coaly material and represent a facies (40,41) not common in the Appalachian Basin. The more woody-coaly facies at P-1, I-3, and I-2 suggest a very local source of nonmarine organic matter as well as nonmarine clastics from the Cincinnati Arch east of P-1. From the cross section (Figure 6) it appears that there is a general progression in kerogen types stratigraphically. In the Frasnian (Wells P-1, I-1 and O-1) the sediments were receiving virtually no structured (woody-coaly) material. The area around Well P-1 was the first to feel the influence of the emergent Cincinnati Arch since at the outset of the Famennian, the organic matter became virtually all structured (facies 00). In the areas of Wells I-1 and O-1, there still was no woody-coaly material well up into the Famennian. The organic matter being incorporated into Wells I-2 and I-3 was for the most part more structured, but obviously not because of a contribution of land plants. This was primarily a marine environment. It seems more likely that the woody material described in these wells was structured material from the stalks and stems of marine plants. The amount preserved in the sediments was dependent on the environment of deposition; when stagnant, restricted-marine conditions prevailed, more organic matter was preserved, whatever its type.

From the kerogen data and the biostratigraphy it appears that during the Late Devonian the Illinois Basin developed as follows: A marine environment prevailed over much of the basin at the beginning

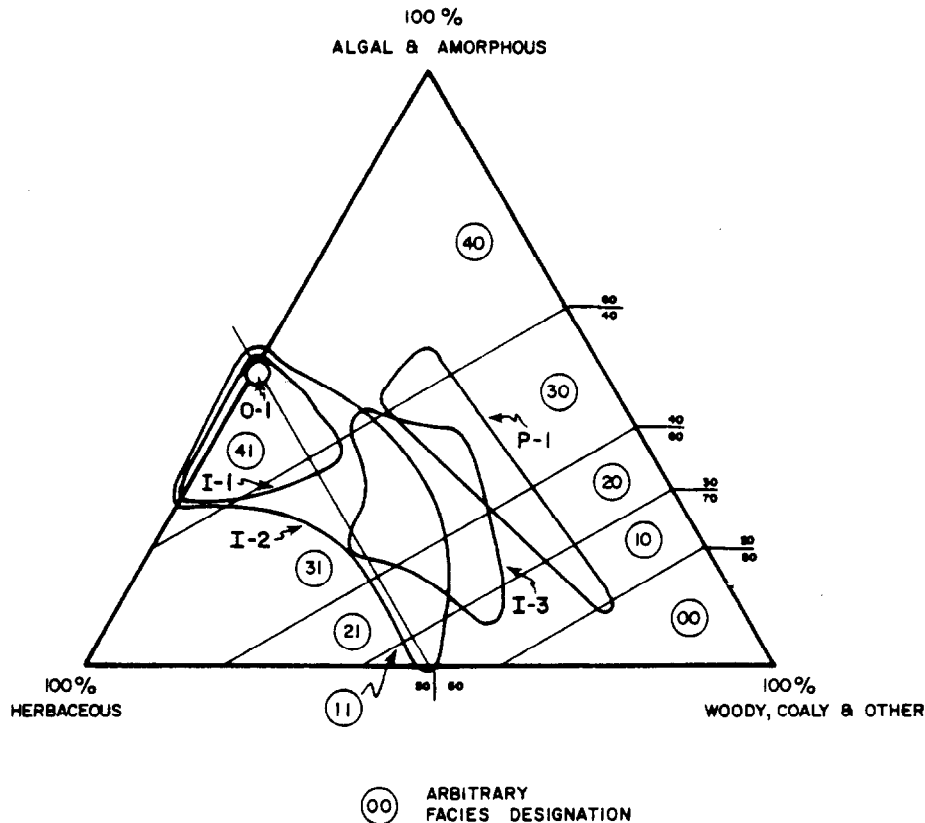


FIGURE 8 - Kerogen facies - Illinois basin wells.

of the period, but in the south and central portions (I-1 and O-1), the waters soon became stagnant; algae bloomed; and relatively large amounts of spores, pollen, cuticular material, etc., were carried in from a local source and were deposited and preserved. The influence of the Cincinnati Arch was first felt at P-1, at the beginning of the Famennian, as nonmarine clastics poured in at this locality from the east. Restricted marine conditions persisted in the areas around I-1 and O-1, and consequently more of the organic detritus was preserved. To the northwest on the northwest shelf (I-3 and I-2), marine conditions dominated caused, probably, by a marine waterway

to the northwest. When conditions became more restricted, more of the biomass, particularly structured marine plant parts, was preserved. But the northwest connection to the open sea closed in very Late Devonian time, as the whole region emerged, and nonmarine conditions took over the whole basin at the close of this period.

The Appalachian Basin also shows very localized organic sources. The organic matter in VA-1 is uniformly mostly woody-coaly facies 00, 10, and 20. This reflects the dominant influence of the nearby Appalachian source area with land-derived structured organic matter and reworked coals from rapidly eroding older

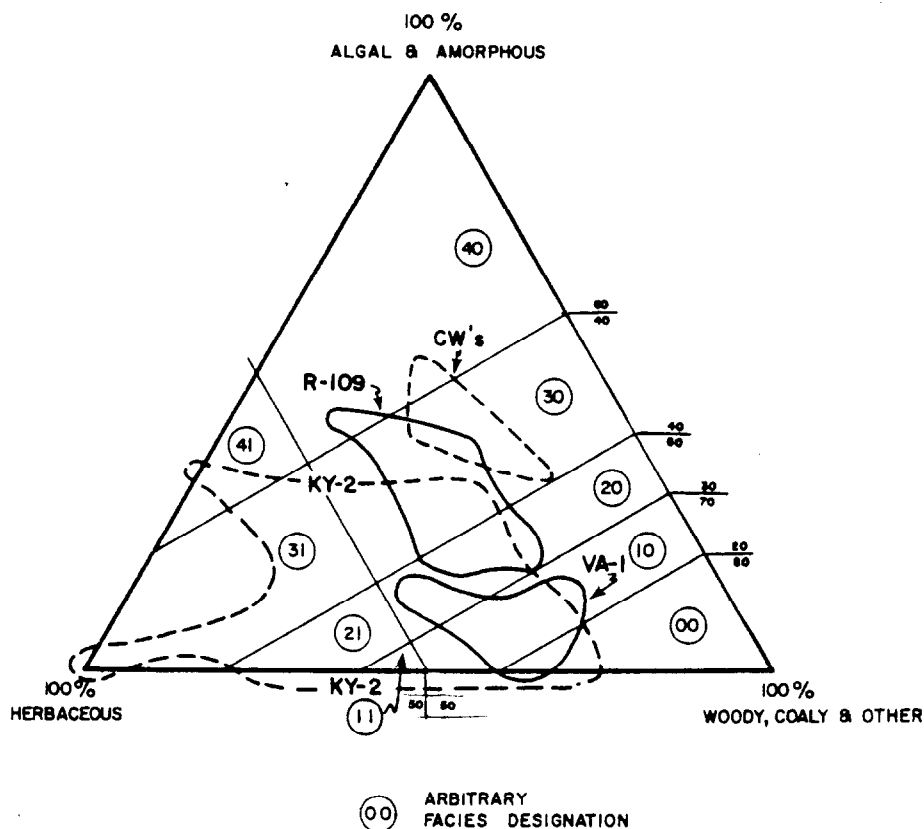


FIGURE 9 - Kerogen facies - Appalachian basin wells.

Paleozoic rocks being dumped into the area. Although some kerogen with an identical makeup was deposited intermittently at KY-2, some of its samples contain a very herbaceous kerogen facies (11, 21, 31, and 41 types), mostly associated with restricted marine conditions. Also interspersed down Well KY-2 there are more algal types, 20 and 30, than are found at VA-1. The kerogen facies at the R-109 and Cottageville wells are more algal or amorphous - 20's, 30's, and even 40's.

These results suggest that there were three different sources of organic matter

during deposition of Late Devonian-age sediments in the Appalachian Basin: woody-coaly from the Appalachian mountains, which are also the source of most of the nonmarine clastics in the basin; amorphous-algal from the open-sea connection to the north; and a less important, very local herbaceous source providing material to the area around KY-2. This local source may have been to the west of KY-2 and is likely to have been the source of herbaceous matter in somewhat lesser amounts in Wells O-1 and I-1 in the Illinois Basin and R-109 in the Appalachian Basin.

If the results of the two basins are considered together, it appears that there were four organic source types: algal-amorphous types from the marine connections to the north, blanketing the whole Illinois basin but only the northern part of the Appalachian Basin; herbaceous, from the low-relief arches separating the basins, with the richest source closest to KY-2, but affecting virtually all the area because the products were easily transported; woody-coaly, particularly from the Appalachians to the southeast, especially dominating deposition at VA-1 but also an intermittent influence at KY-2; and an abundance of a conjectured structured marine-plant material in the northwestern Illinois Basin. No matter what the source of the organic matter, preservation was enhanced if the environment at the time of deposition was restricted marine.

Kerogen alteration indices and vitrinite reflectance

The extent of hydrocarbon generation of potential source rocks is controlled by their thermal history. Two methods, kerogen coloration and vitrinite reflectance, were used to measure the thermal alteration of the Devonian shales. The kerogen coloration of the plant cuticle and spore-pollen debris was measured in transmitted light. Unaltered kerogen is light greenish yellow (Stage 1 Thermal Alteration Index, or TAI); severely altered kerogen is black (Stage 5); and intermediate stages range from orange through dark brown. The oil-generation stages correspond to moderately mature to mature kerogens which are yellow-orange to light brown color (Stages 2 to 3-).

Vitrinite reflectance (R_o), i.e., reflectivity of the small organic grains exposed on a polished surface, was also used to measure the degree of thermal alteration. It is generally accepted that R_o values ranging from 0.2 to 0.6 indicate that the sediments are too immature for oil generation. However, our work strongly suggests that in Paleozoic rocks, the organic matter is exposed to thermal stress for relatively longer times, and therefore, the onset of significant generation may occur at somewhat lower values; e.g., 0.4. Elsewhere, the zone of petroleum generation is usually interpreted to fall in the range from 0.6 to 1.2, and values from 1.2 to 3.0 generally indicate a thermal history sufficient to form wet gas and methane. The severely altered or metamorphosed organic matter represented by R_o values greater than 3.0 is considered to indicate organic matter that has exhausted its capacity to generate significant hydrocarbon. If the liquid-generation boundary is shifted downward, as we propose, the other ranges (e.g., for mature gas only) would also be shifted downward.

The thermal histories of the Devonian shales in all but one (VA-1) of the wells analyzed in this study are very uniform. The organic matter in the shales from seven of eight wells in which the kerogens were analyzed is characterized by its yellow to orange-brown color. This coloration is consistent with a thermal alteration index of Stage 1+ to 2. The average value of Stage 2 corresponds to a thermal history equal to the early stages of petroleum generation. The average vitrinite reflectances in Wells I-2, I-3, P-1, I-2, and O-1 are between 0.45 and 0.50. In the KY-2 well, a slightly higher

thermal alteration corresponding to a mean average R_0 of 0.52 was measured. The mean average R_0 for vitrinite particles in the R-109 well was 0.70, and in the VA-1 well, about 1.0.

Thus, in the Illinois Basin the vitrinite reflectance values suggest that these rocks are not quite mature enough to have generated large quantities of hydrocarbons; the kerogen coloration indicates they have just begun doing so. In the Appalachian basin, there is increasing thermal maturity, and hence probable hydrocarbon generation, an interpretation consistent with kerogen coloration. It should be noted that the individual measurements of R_0 in any sample vary widely; in fact, the spread in values may be caused by two contributions of organic matter: one, less mature, preserved from living matter contemporaneous with sediment deposition, and a second, more thermally altered, reworked organic matter from older sediments once buried more deeply to the east, uplifted with the sediments, and eroded and carried out into the Appalachian geosyncline to be redeposited. This reworked, probably oxidized, redeposited organic material has much less potential to generate hydrocarbons than ordinary once-deposited kerogen.

Core gas analysis

At the well site, the core sample is removed from the barrel, cleaned, and examined prior to being canned in a gas-tight container. The first test performed on the sample when it is brought to the laboratory is an analysis of the gas in the headspace of the sample container. The subsequent analysis is that of the residual gas remaining in the core. The two results are combined to yield a

minimum value of total gas present in the sediment. In spite of a whole host of uncontrolled variables that must be contended with (i.e., widely varying time between coring and sample canning, care in collection, different volumes collected, variable lithologies, etc. that determine the percentage of gas retained in the sediment), gas content has proven to be an extremely important assessment parameter. The total amount of gas generally indicates overall hydrocarbon-potential realization, and the abundance of ethane and heavier hydrocarbon homologs in the gas indicates how liquid prone (in contrast to exclusively methane gas prone) the rocks are.

The gas results, from these basins, are somewhat inconsistent with the other analyses, and perhaps they simply reflect the quality of sample; i.e., some that ought to contain more gas based on their organic carbon contents may be low because of long time periods that elapsed between coring and sealing in the cans. Well I-2 may be an example of this. Even in samples in which the organic carbon content was two and three percent, only about 20,00 ppm gas was present. On the other hand, in these sediments at such relatively shallow depths, the gas may simply not be retained, having escaped vertically through the thin sedimentary cover. It was apparently generated because of thermal exposure, because the gas wetness (C_2+ in the total C_1-C_4) reaches 80% in the richest cores. Such values are only observed well within the thermal zone of oil generation (Stage 2 TAI and higher). In fact, it is these high gas-wetness values that suggest that although the kerogen is at marginal TAI's and the R_0 's too low for the material to have experienced the oil-generating stage,

that in these relatively older rocks, the long exposures have compensated for the lower temperatures experienced by the rocks. Another alternative is that the gas has migrated upward from more thermally altered, older rock units. This latter alternative seems unlikely, as will be shown later.

East of I-2, at Well P-1, the three gas samples are quite variable, but the one value of 270,000 ppm (total gas) at 2521 ft indicates a good, prolific hydrocarbon source; its wetness of only 27% suggests a primarily gas-prone facies, which is inconsistent with the type of organic matter (kerogen type 40) that is normally more prone to generate liquids and wet gases. Greater gas wetness (86% and 73%) is observed in the smaller amounts of gases in the samples above and below the anomalous one.

At Well I-1, the samples all had large volumes of gas (340,000 to 560,000 ppm), also indicating prolific hydrocarbon sources, marginally liquid prone (25% to 40% ethane and heavier homologs in the $C_1 - C_4$ gas). At Well O-1 the sediments are also good hydrocarbon sources (230,000 ppm to 410,000 ppm), and are also marginally liquid prone in the upper samples (26% to 35% C_2+) to very gas prone in the older ones (15% C_2+).

The interesting point is that these gas wetness results are consistent with the kerogen facies discussed earlier. Those samples in the 40 and 41 facies tend to have less ethane and higher homologs in gas than those in the 10, 20, and 30 kerogen facies. This is contrary to the generally accepted idea that the reverse should be the case. This deserves more extensive study.

In the Appalachian Basin, at Well R-109, the samples are rich in gas volumetrically up to 3 million parts gas per million parts sediment (because of gas compressibility, a unit volume of rock at subsurface conditions can contain enough gas so that it will expand to more than the volume of rock when brought to the surface; i.e., at atmospheric pressure). There is a close correlation of higher gas contents with higher organic carbon content. The gas is wet (62% to 84% C_2+), which is very high for the low kerogen TAI's and R_0 's of the vitrinite. Again, this suggests that there is a trade-off of time for lower temperatures (at least indicated by kerogen properties) in these old, Paleozoic, rocks. In Well KY-2, gas contents are about an order of magnitude lower than in R-109, but the host rocks would still be classed excellent potential sources of hydrocarbons by our criteria. In this well also there is a very good correlation of higher gas contents with higher organic carbon values. The wetness values vary considerably but are mostly in the 50% to 60% C_2+ range, i.e., definitely liquid prone. In Well VA-1 the gas contents are very high. They are as high as at R-109 and correlate directly with organic carbon content, but they are very low in C_2+ contents (7% to 18%), indicating an almost exclusively gas facies, consistent with the predominance of woody-coaly kerogen.

Perhaps the most important indication of the gas analyses, beyond the fact that the sediments are generally very gassy, is that the gas apparently does not migrate very far in these fine-grained sediments, especially those at depths greater than 2000 ft. This can be shown best on a plot of gas contents as a function of organic carbon contents (Figure 10). For

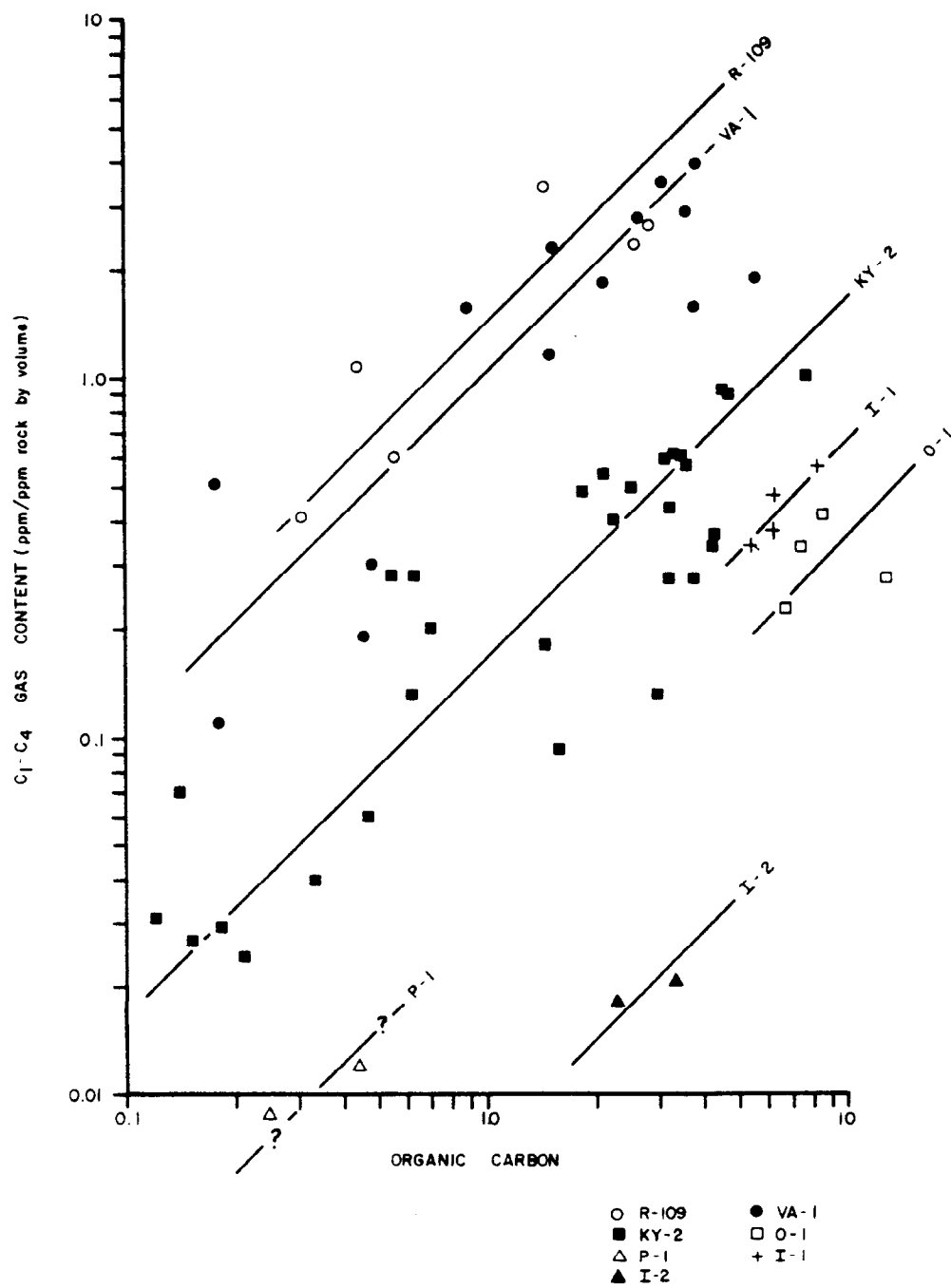
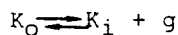


FIGURE 10 - Correlation of C₁-C₄ gas contents with organic carbon contents in various wells.

each well there is a good linear correlation, but the intercepts are different. The organic matter in Wells R-109 and VA-1 is apparently the gassiest. Samples from KY-2 contain about an order of magnitude less gas per unit of organic matter; and Wells I-1 and O-1 have even less gassy organic matter. I-2 appears even lower on the plot but, as discussed earlier, this may be due to gas loss at shallow depths of burial. The excellent correlation of gas content to organic carbon content suggests that the gas is indigenous and that, as it is formed, it is essentially trapped right in the pores where it is formed. There must be virtually no permeability to allow the gas to spread out in the section. Therefore, with the stimulation methods being considered, it appears that maximum gas recoveries will be from the richest organic facies. Fracture networks that coincide with or are contiguous to these facies should be sought. Furthermore, as indicated earlier, these generally coincide with or are stratigraphically close to sediments deposited in the restricted marine environments.

The retention of gases and the apparently low R_o and TAI values may not be totally unrelated. There has been speculation among organic geochemists of the differences that might be observed between those natural rock-organic matter systems in which the gas is retained and those in which the gas is transported or migrates away. In the reaction



(K_o indicates the original kerogen and K_i the product kerogen from which gas (g) has been thermally cracked), if the gas

is retained in the system and if there is an equilibrium, the kerogen would not alter to as "mature" TAI and R_o values as it would if the gas were able to diffuse from the reaction site and away from the kerogen. Actually, the C_{15+} hydrocarbon data suggest that the liquid as well as the gaseous hydrocarbons are retained at their sites of formation.

C_{15+} hydrocarbon contents

Another standard method of appraising the hydrocarbon potential of sediments is the extraction of soluble bitumen and separation of the hydrocarbons and determination of their concentrations. A useful method of delineating regional or stratigraphic trends in potential and of distinguishing various wedges of different composition is a plot of heavy hydrocarbon contents as a function of organic carbon contents. This presentation is included for the Illinois Basin (Figure 11) and the Appalachian Basin (Figure 12). The figures are divided into nine arbitrary facies for purposes of plotting on the cross sections. Clastic rocks with less than 0.4% organic carbon (facies 00, 10, and 20) do not have enough carbon to be considered potential sources of producible hydrocarbon. Above approximately 1.5% organic carbon, the rocks have relatively great hydrocarbon-source potential. Thus, for the most part, this criterion establishes the obvious, that much of the Devonian dark shale of these two basins is a potential source, albeit a quite variable one.

The amount of hydrocarbon relative to the organic carbon content provides another useful guideline, the greater the ratio, the greater the tendency for the rock to

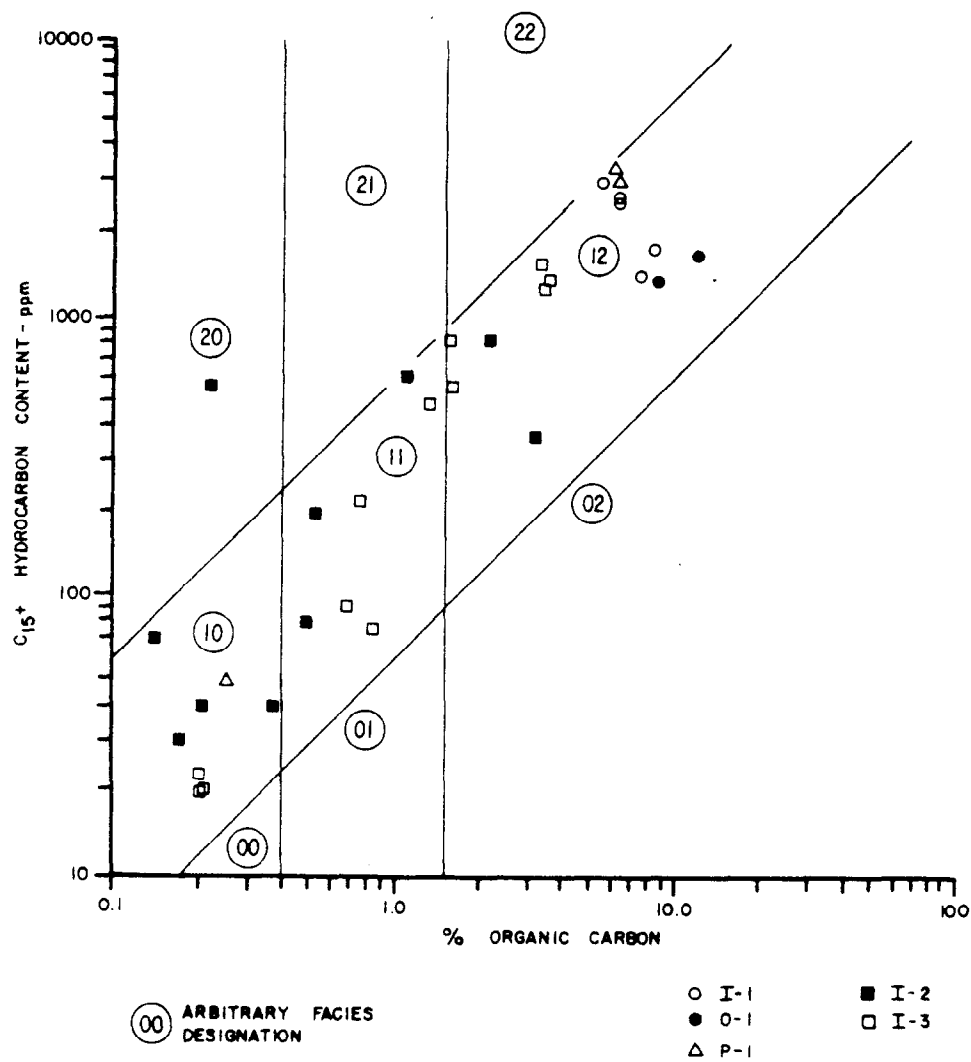


FIGURE 11 - Organic facies - Illinois Basin wells.

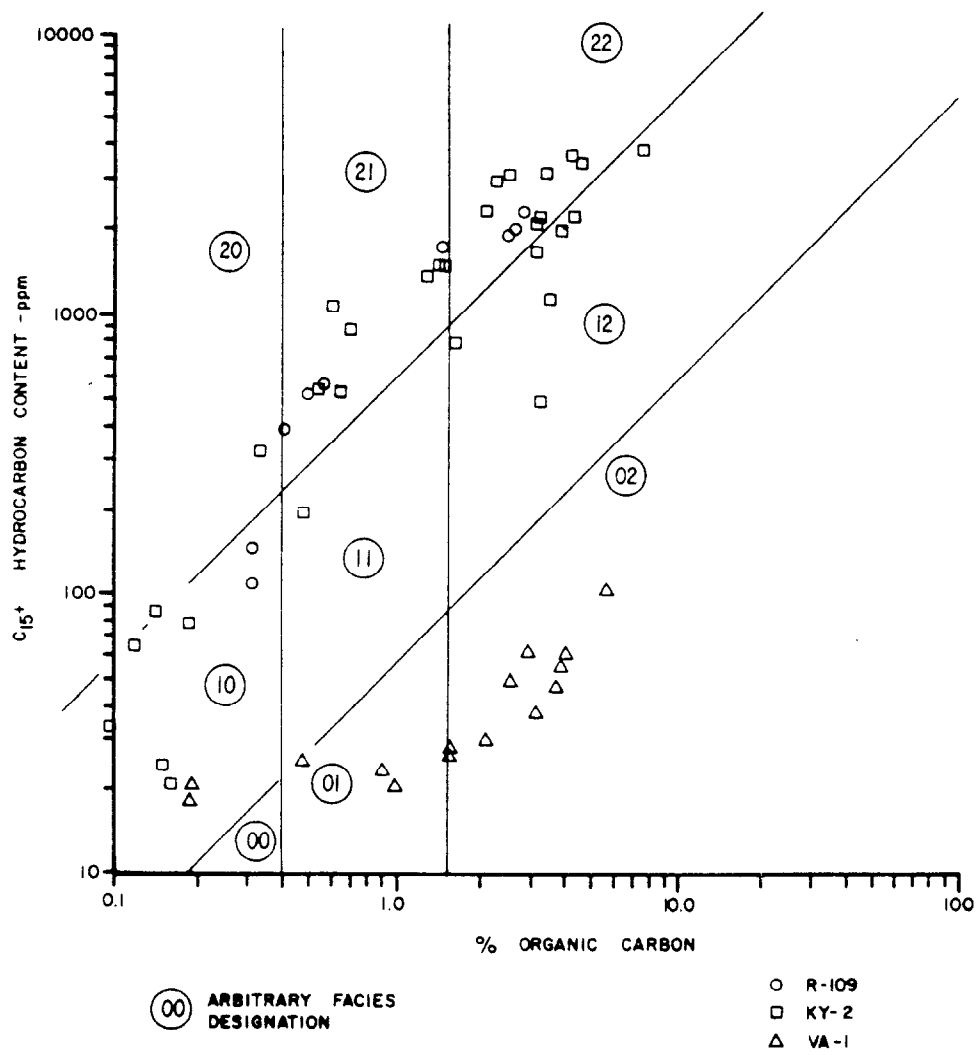


FIGURE 12 - Organic facies - Appalachian Basin wells.

give up liquids. In fact, at ratios below about 100 ppm hydrocarbon per percent organic carbon, or twice as high as the ratio (the line) dividing facies 00 - 02 and 10 - 12 (which is about 50 ppm hydrocarbon per percent organic carbon), rocks are labeled "gas - only". Therefore, on the diagrams, data points of the 00, 01, and 02 facies types are definitely dry-gas (virtually only methane) prone. Notice that this includes most of the samples from the VA-1 well. Those few samples above the line are so low in organic carbon and hydrocarbon they can be ignored for all intent and purpose and can be considered nonsources. This further points up the very unique character of the organic matter in this locality. It is a more thermally altered, more woody-coaly, nonmarine, gassy (Figure 10) type of organic matter, obviously sourced in the Devonian version of the Appalachian mountains nearby.

A straight line with a slope of 1 can be fitted to the data from each of the wells. (As was pointed out earlier, probably most of the data falling in fields 00 and 10 should be ignored because the scatter of analytical data here is usually considered to be an artifact; it reflects the decreasing analytical accuracy and precision at lower hydrocarbon and organic carbon contents.) The straight-line relationships strongly suggest that there may be only three basic types of hydrocarbon facies in these two basins; a dry-gas Southern (probably east of the basin axis) Appalachian type; a more liquid-prone Illinois Basin type; and a still more liquid-prone, Northern Appalachian Basin type.

Another important observation is that the ratio for each family persists even at

lower organic carbon contents. This shows that migration of heavier hydrocarbons from richer to leaner shales does not generally take place; the hydrocarbon appears to be locked in place. The most likely exception is one sample from the I-2 well whose C₁₅+ hydrocarbon content is quite high for its organic carbon content. In fact, the sample is at 538 ft. The next deeper sample contains about the same amount of hydrocarbon but five times as much organic carbon. This may be a rare case of redistribution of C₁₅+ hydrocarbon in the sediments included in this study. Furthermore, the particular 'enriched' sample also contains more C₁ - C₄ gaseous hydrocarbons than either of its neighbors, 10000 ppm versus 6400 ppm and 2400 ppm respectively, which further supports the interpretation that in this one case there was migration of both hydrocarbons to a slightly more porous zone.

The absence of overlap of data fields between the samples from VA-1 and KY-2, particularly, suggests that although marine, restricted marine, and nonmarine environments of deposition alternated in various parts of the basins, and although the heavier, particulate portions of the organic matter (kerogen) are very closely related to, if not controlled by, localized source provinces, the heavy hydrocarbon precursors are independently formed and geographically localized. Thus, we may have regional solid-matter (kerogen) organic facies superimposed on a more variable, environmentally controlled, hydrocarbon-organic matter facies.

In support of the previous conclusion the coincidence of the 02, 12 and 22 facies on the cross section with the richest organic carbon zones and thus the restricted marine environments is striking. No matter

what type organic matter may have existed in a particular basin position, more of it was preserved and deposited in the sediment when the environment was restricted marine. Less of any type of organic matter was present in the sediment if the conditions were either marine or nonmarine. Therefore the environmental control appears to be the overriding one determining the amount of organic matter incorporated in the sediments of these two basins.

More study is needed on this apparent dual control of organic facies: what caused the two types, what relationship they bear to the gas content in the sediment, and whether they can be projected to or predicted in undrilled portions of the basin. Both facies provide constraints on certain other important aspects of the problem. For example, only samples with greater than 3% organic carbon and 350 ppm C_{15+} hydrocarbons (i.e., Illinois Basin-type facies) will yield more than 5 gal/ton of hydrocarbon liquids upon material balance assay or thermal extraction analysis. On the other hand, only samples with greater than 28% Amorphous-Algal and less than 35% woody-coaly kerogen types will give as great yields.

Carbon isotope ratios

One of the perplexing results from the geochemical studies is the C^{13}/C^{12} carbon isotope ratios [expressed as differences in parts per thousand from an arbitrary standard the Peedre belemnite (PDB)]. Although only relatively few analyses have been run, the results do not agree with the widely accepted view that carbon from more-marine environments is heavier (smaller negative numbers in our

scheme of presentation). To illustrate this discrepancy, a sample from the P-1 well had a value of -24.6 vs PDB, and another in the VA-1 well, -25.6, coincident with a nonmarine environment of deposition, whereas several others from marine environments were lighter (more negative), and the lightest, -31.6, was from a restricted environment.

Moreover, within each one of the three "facies" indicated by the three distinct HC/OC ratios in the three geographic areas, the samples richest in absolute amounts of both hydrocarbon and organic carbon have the lightest carbon. For example, for the Illinois Basin type, the $\delta C^{13}/C^{12}$ values are -24.6 for the lean sample from Well P-1, and from -28.0 to -31.6 for several rich samples from Wells P-1, I-1, and O-1; for the northern Appalachian Basin type, the values range from -26.7 for a low-hydrocarbon, low-organic carbon sample to -28.9 to -30.2 for richer samples, all from Well KY-2. The trend is not so clear-cut with the Southern Appalachian Basin type: -25.6 for the leanest sample in Well VA-1 to -27.9 for the richest, but with three intervening samples ranging from -28.1 to -29.3. If the isotope ratios are considered along with the triangular diagrams showing a relative kerogen type distributions, our preliminary results also contradict the long-accepted view of the more marine the organic matter, the heavier the carbon isotopically. For Well P-1 (in particular) and Wells VA-1 and KY-2, the greater the proportion of woody-coaly kerogen, the heavier the carbon (less negative $\delta C^{13}/C^{12}$ values). Whatever the cause of these unusual trends in the carbon isotope composition, it merits much more work to document and explain it. The results will be of great interest to organic geochemists in general.

Future work

This study demonstrates the utility of the more general types of organic geochemical data in augmenting reconstructions of basin geology, environments of deposition, source provenances, etc. It also shows how organic geochemistry provides unique information bearing on the resource potential of sediments and sedimentary sections. The data show how rapidly, i.e., in how narrow a stratigraphic interval, organic contents and facies can change in a basin, particularly at an active basin position such as a hinge line or inflection point (Well KY-2) between shelf and deeper basin. Therefore, the work provides a strong case for closer sample spacing. The fact that the full organic-rich cycles were not sampled (Cottageville Wells, and Wells KY-2, VA-1 I-3, P-1, I-1, and O-1) provides strong justification that in future wells samples be taken to cover the entire "dark shale" unit and the less-rich geologic section both above and below it. For total resource evaluation, this additional sampling, to bracket all the organic-rich zones, would seem to be necessary.

Secondly, at more closely spaced, regular intervals (e.g., every 10 ft) in every well drilled in the future, a full suite of comprehensive geochemical and geological analyses are needed to give a more detailed picture of the location, the character, and the continuity of the gas-rich zones. In some wells, the age and environment can only be speculated now, or projected from wells over 50 miles away.

This short study should be followed with a study of the more detailed aspects of the organic geochemical data and the

importance and relationships of other variables. In particular, the molecular compositions of the hydrocarbons merit much more attention. Moreover, the geochemical, lithological, and mineralogical data need to be correlated with the geology of the study area being conducted by other investigators. For example, what is the association between the organic-rich zones and the naturally fractured zones?

Finally, carbon isotopic composition of organic matter in samples closely spaced across depositional-environment boundaries should be carefully analyzed to confirm and, we hope, to explain the apparent contradictory picture that these data give with respect to the accepted relation of isotope ratios to environment of deposition and type of organic matter. Geochemically, this may be the most important discovery of this study.

References

1. S. J. Martin, "Hydrocarbon Evaluation Study of Shales from Wells #R-109, #12041 and #11940," Geochem. Laboratories, Inc. Report (October 1976).
2. R. E. Zielinski, "Physical and Chemical Characterization of Devonian Gas Shale, Quarterly Status Report (February 15-March 31, 1977)," MLM-ML-77-43-0002 (April 1977).
3. R. E. Zielinski, "Physical and Chemical Characterization of Devonian Gas Shale, Quarterly Status Report (April 1-June 30, 1977)," MLM-ML-77-46-0001 (July 1977).
4. R. E. Zielinski, "Physical and Chemical Characterization of Devonian Gas Shale, Quarterly Status Report

(October 1-December 31, 1977),"
MLM-ML-78-41-0002 (January 1978).

5. R. E. Zielinski, "Characterization of the Devonian Shales in the Appalachian Basin," Third ERDA Symposium on Enhanced Oil and Gas Recovery and Improved Drilling Methods, The Petroleum Publishing Company, Tulsa, Oklahoma (August 1977).
6. R. E. Zielinski and S. J. Martin, "Thermal Maturity and Organic Facies of Devonian Shales from Selected Wells," Third ERDA Symposium on Enhanced Oil and Gas Recovery and Improved Drilling Methods, The Petroleum Publishing Company, Tulsa, Oklahoma (August 1977).
7. R. E. Zielinski, "Geochemical Characterization of Devonian Gas Shale," presented at the First Eastern Gas Shale Symposium, Morgantown, West Virginia, October 17-20, 1977.
8. R. E. Zielinski, et al., "Physicochemical Characterization of Devonian Gas Shale," presented at the First Eastern Gas Shale Symposium, Morgantown, West Virginia, October 17-20, 1977.

Distribution

EXTERNAL

TIC, UC-92 (230)

Technical Report Library, Monsanto, St. Louis
R. K. Flitcraft, Monsanto Research Corporation
H. N Hill, DOE/Dayton Area Office
R. D. McIver, Geochem Research Inc. (25)
Morgantown Energy Technology Center (200)

INTERNAL

W. T. Cave
V. M. Franchetti
C. W. Huntington
L. V. Jones
E. W. Johnson
B. R. Kokenge
R. J. Larson
J. R. McClain
S. W. Nance
W. D. Pardieck
P. W. Seabaugh
G. R. Sundheimer
R. E. Zielinski (25)
Library (15)
Publications